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Development of Textile Composites Impregnated with Dicyclopentadiene Resin

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ABSTRACT

In order to exhibit the high performance by the perfect impregnation of matrix, the dicyclopentadiene resin with high fluid performance at liquid state has been applied to the textile composites. Since the dicyclopentadiene resin has not ever been used for matrix of fiber reinforced composites, the foundational mechanical properties of plain woven fabric composite with the dicyclopentadiene resin were investigated. Especially, to catch the effect of interfacial state between glass fiber and dicyclopentadiene resin, uni-axial tensile and 3-point bending tests were carried out for 4 kinds of specimens treated by different silane coupling agents. And the microscopic failure states under tensile load were observed by SEM. Furthermore, the mechanical properties of dicyclopentadiene based composites were compared with unsaturated polyester based composite. From the experimental result, it was recognized that the conventional silane coupling agents are not effective for glass / dicyclopentadiene composite. Therefore, the dicyclopentadiene based composite has inferior bending properties although it has superior tensile performance to the unsaturated polyester based composite.

1. INTRODUCTION

Textile composite materials have been widely applied to a lot of structures. Textile fabrics can give us three dimensional material design which is impossible by laminated composites, and they are expected to exhibit more excellent mechanical performance [1-3]. As these composites designed for multiple performance have the complicated fabric architecture, it is difficult to impregnate the inside of material with matrix resin perfectly [4]. In fact, the functional properties of the textile composites are decreased by many voids which cause high stress concentration and cracks. In order to fabricate textile composites as designed for multiple performance, the voids should be extinguished by the perfect impregnation with matrix resin. In this study, a new multipurpose high performance resin, which is called dicyclopentadiene, has been applied to the textile composites.

Although the dicyclopentadiene resin was produced early in industry, its molding with additives such as fiber reinforcement was impossible. In recent years, the new catalyst technology has been developed by Grubbs [5] and Schrock [6]. By using this new ring-opening metathesis polymerization catalyst, the dicyclopentadiene resin became possible to be mixed with additives and create very tough cross-linked molded compounds in air atmosphere [7,8]. The most remarkable advantage of dicyclopentadiene resin is to make it all possible to manufacture mechanically strong molded products like engineering plastics from low viscous liquid monomers. Table 1 shows the mechanical properties of the dicyclopentadiene resin compared with other conventional thermosetting resins. Although the viscosity of dicyclopentadiene resin is remarkably low, the elastic modulus and strength keep the approximately same value with other resins.

Table 1 The comparison of mechanical properties among the dicyclopentadiene and the conventional thermosetting resins

	Dicyclopentadiene	Vinylester	Epoxy
Viscosity (mPa.s)	5.00	330	720
Tensile modulus (GPa)	—	3.60	3.05
Tensile strength (MPa)	58.0	64.0	66.0
Flexural modulus (GPa)	2.40	3.90	3.29
Flexural strength (MPa)	104	120	116

Therefore, the dicyclopentadiene resin can be considered to have the possibility to provide the large improvement of mechanical performance of textile composites.

Since the dicyclopentadiene resin have not ever been used for matrix of fiber reinforced composites, the foundational mechanical properties of glass plain woven fabric composite with the dicyclopentadiene resin were investigated as the first step of this research. The mechanical properties of composites are affected strongly by the interfacial adhesive properties between fiber and resin which depend on the surface treatment of fiber. In order to catch the effective surface treatment for the dicyclopentadiene resin, uni-axial tensile and 3-point bending tests were carried out for 4 kinds of specimens treated with different silane coupling agents. And the microscopic failure states under tensile load were observed by SEM. Furthermore, the mechanical properties of dicyclopentadiene based composites were compared with unsaturated polyester based composite in order to confirm that the resin is more effective for textile composite than the other conventional resins.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

Material used for this research was E-glass woven fabric reinforced dicyclopentadiene. The matrix was the standard type of Metathene™ (Hitachi Chemical Co., Ltd., Japan). The reinforcement was a glass plain woven fabric (Nitto Boseki Co., Ltd., Japan) which has 44 warp strands and 34 weft strands per 2.5 cm. One strand consists of 4000 filaments whose diameter is 9 μm. The surface of glass fibers was treated by 4 kinds of silane coupling agents as shown in table 2. The concentration of all silane coupling agents were 0.4 wt%. Composite laminates with 10 layers were fabricated by hand lay up molding method. For the purpose of gelation, the laminates were kept at 40°C for 2 hours, at 20°C for 1 hour and at 140°C for 1 hour in sequence.

Table 2 The silane coupling agents used for surface treatment of glass fiber

Coupling agent	Chemical formula
Methacryl silane γ-Methacryloxypropyltrimethoxysilane	$\begin{array}{c} \text{CH}_2 = \text{C} - \text{C} - \text{O}(\text{CH}_3)_3\text{Si}(\text{OCH}_3)_3 \\ \quad \parallel \\ \text{CH}_3\text{O} \end{array}$
Epoxy silane γ-Glycidoxypropyltrimethoxysilane	$\begin{array}{c} \text{CH}_2 - \text{CH} \text{---} \text{CH}_2\text{O}(\text{CH}_3)_3\text{Si}(\text{OCH}_3)_3 \\ \diagdown \quad \diagup \\ \text{O} \end{array}$
Vinyl silane Vinyltris (β-methoxyethoxysilane)	$\text{CH}_2 = \text{CHSi}(\text{OC}_2\text{H}_5\text{OCH}_3)_3$
Amino silane γ-Aminopropyltriethoxysilane	$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$

Figure 1 shows the dimension of specimens used for uni-axial tensile and 3-point bending tests. The longitudinal direction of specimen was matched with the fiber direction of weft. Both tensile and bending tests were performed as controlling the displacement of cross-head at speed of 1.0 mm per minute by using Instron universal testing machine. In 3-point bending test, the distance of span was fixed at 32 mm.

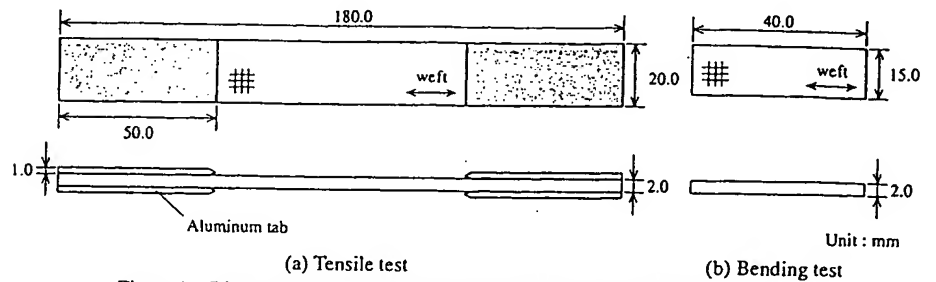


Figure 1 Dimension of specimens for uni-axial tensile and 3-point bending tests

3. RESULTS AND DISCUSSION

Figure 2 shows the experimental results for relation between tensile stress and strain of each silane-treated specimen obtained by uni-axial tensile test. From this figure, it can be confirmed that vinyl silane-treated specimen has the highest tensile modulus and strength. Methacryl silane-treated specimen indicates the similar tendency to epoxy silane-treated specimen. Amino silane-treated specimen is inferior to the other specimens. Figure 3 shows the comparison of tensile properties among dicyclopentadiene based composites treated by different silane coupling agents. In order to catch the relative performance for the conventional resin based composites, the properties of vinylester based composite treated by methacryl silane coupling agent are also shown in this figure. Methacryl silane coupling agent has been reported to be the most effective for glass fiber reinforced vinylester resin [9]. Although the dicyclopentadiene based composites are inferior to the vinylester based composite in tensile strength, they have superior tensile modulus to the vinylester. Especially, the vinyl silane-treated specimen attains approximately 30% increase of tensile modulus compared with the vinylester based composite.

Figure 4 shows the experimental results for relation between bending stress and strain of each silane-treated specimen obtained by 3-point bending test. The effect of silane coupling agents on the bending properties can be considered to be similar to tensile properties. The initial bending modulus doesn't have the remarkable difference among all silane-treated specimens. On the other hand, the bending strength depends strongly on silane coupling agent. Vinyl silane-treated specimen has the highest strength, and amino silane-treated specimen is inferior to the other specimens. Figure 5 demonstrates the comparison of tensile properties among dicyclopentadiene based composites treated by different silane coupling agents and vinylester based composite. From this figure, it can be recognized that all of dicyclopentadiene based composites are inferior considerably to vinylester based composite.

In order to reveal the effect of silane coupling agent on interfacial adhesion between glass fiber and dicyclopentadiene resin, the microscopic failure states of broken specimens after tensile test were observed by SEM. Figure 6 shows the microphotographs for failure state of each silane-treated specimen. Because the strong adhesion of matrix resin with glass fibers can't be seen in all microphotographs, the debonding is considered to be easy to occur at the interface between fiber and resin. Therefore, it can be guessed that the interfacial adhesive strength in all silane-treated specimens is low and that the silane coupling agents used for this research is not effective for glass fiber reinforced dicyclopentadiene. This is the reason that dicyclopentadiene based composites are inferior considerably to vinylester based composite in bending properties. The specimen under bending load is attacked by tensile, compressive and

interlaminar shearing stresses. In the case of dicyclopentadiene based composites, the interlaminar shearing performance is considered to be decreased by poor interfacial adhesion.

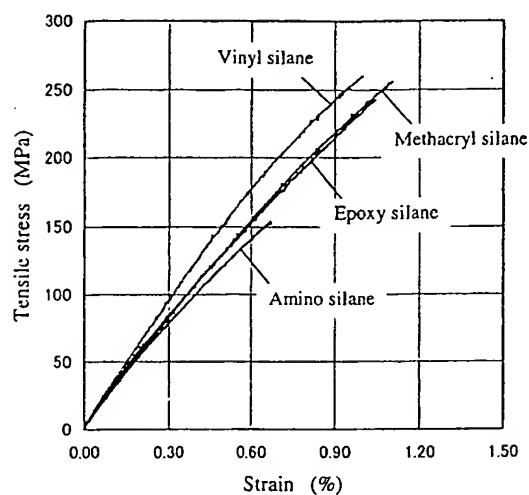


Figure 2 Experimental results for relation between tensile stress and strain obtained by uni-axial tensile test

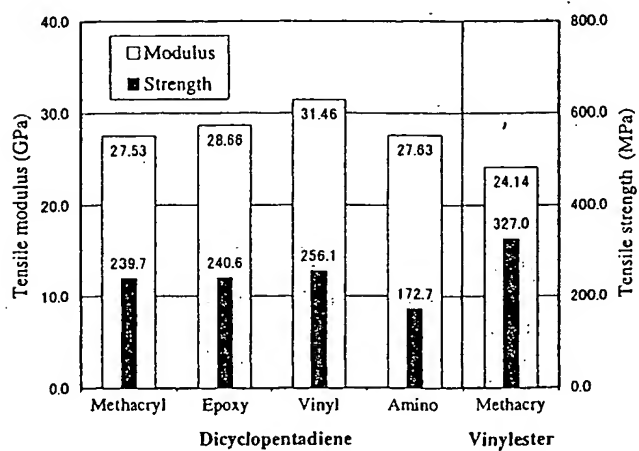


Figure 3 Comparison of tensile properties among dicyclopentadiene based composites treated by different silane coupling agents and vinyl ester based composite

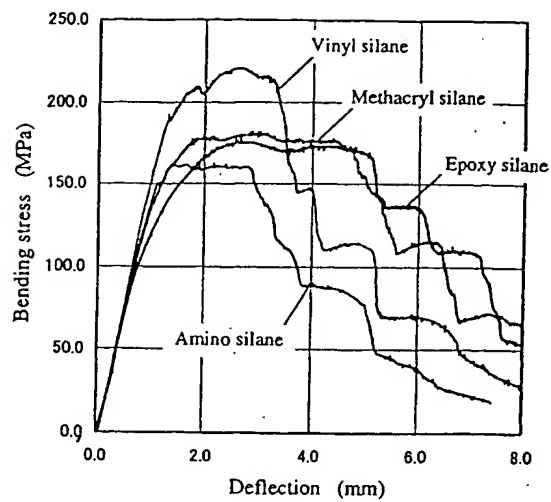


Figure 4 Experimental results for relation between bending stress and deflection obtained by 3-point bending test

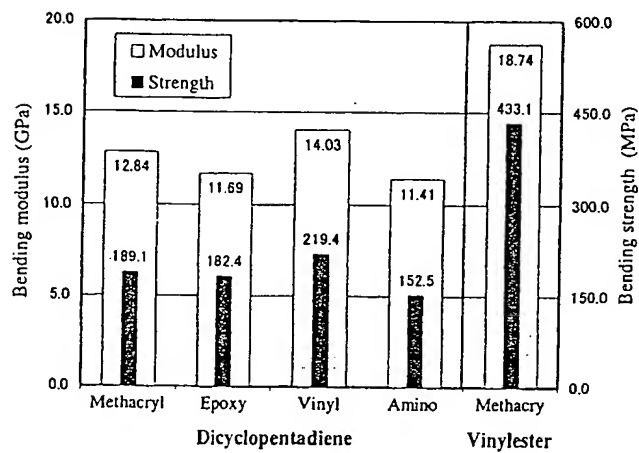
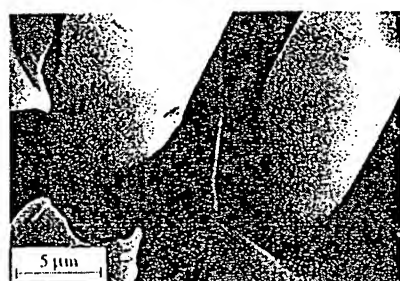
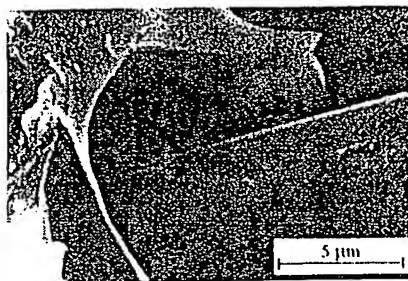


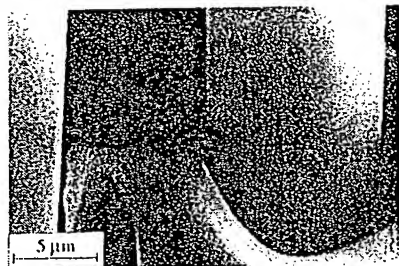
Figure 5 Comparison of bending properties among dicyclopentadiene based composites treated by different silane coupling agents and vinylester based composite



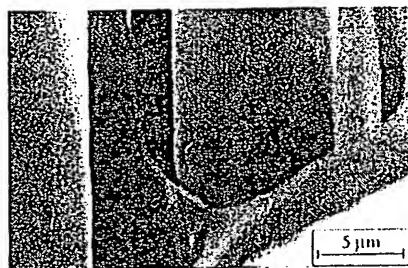
(a) Methacryl silane



(b) Epoxy silane



(c) Vinyl silane



(d) Amino silane

Figure 6 Microphotographs for failure state of each silane-treated specimen after tensile test

4. CONCLUSION

In order to improve the mechanical performance of textile composites by the perfect impregnation of matrix resin, the dicyclopentadiene resin with high fluid performance at liquid state has been applied to the textile composites. In this paper, the mechanical properties of glass woven fabric reinforced dicyclopentadiene resin were investigated by uni-axial tensile and 3-point bending tests. And 4 types of specimens treated by different silane coupling agents were used for this research to catch the effective coupling agent for glass / dicyclopentadiene composite. In result, it was recognized that all of dicyclopentadiene based composites treated by different silane coupling agents have the excellent tensile performance but that they are inferior considerably to the conventional unsaturated polyester based composite in bending performance. From the observation of microscopic failure states by SEM, it was disclosed that the interfacial adhesive strength is poor and that the typical silane coupling agents are not effective for glass / dicyclopentadiene composite. By development of effective coupling agent, glass fiber reinforced dicyclopentadiene is considered to give more excellent mechanical performance.

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